Mechanisms of Arsenate Adsorption by Highly-Ordered Nano-Structured Silicate Media Impregnated with Metal Oxides

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Introduction

Throughout the world, arsenic is creating potentially serious environmental problems for humans and other living organisms. Most reported arsenic problems are found in groundwater water supply systems and are caused by natural processes such as mineral weathering and dissolution caused by the changes of geochemical environments to reductive conditions (*1*, *2*). Arsenic contamination is also caused by human activities such as mining wastes, petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries, and coal fly ash (*3-5*).

Small public water systems will face heavy financial burdens in order to comply with new stringent regulations which will lower the arsenic contamination limit from 50 to 10 ppb (*6*). Because of this, a highly effective, reliable, and economic technique is needed to meet the new arsenic maximum contaminant level. Many adsorbents have been developed as a promising technology for arsenic removal due to their easiness of set up (*2, 7-15*). For the POE/POU (Point of Entry/Point of Use) adsorption system, activated alumina has been one of the best available adsorbents and has been extensively studied because of its effectiveness and selectiveness for arsenic adsorption removal (*7, 16*). However, the highly alkaline feeding solution should be controlled with an acidic solution to have a pH between 5.5 and 6.0 so that optimum arsenic adsorption capacity of activated alumina can be achieved (*17*). When activated alumina was regenerated, its adsorption capacity was reported to be reduced by 30-40% (*18*). Furthermore, due to the slower adsorption reaction, activated alumina requires relatively longer empty bed contact times (3-5 min) than ion-exchange resins (*19*).

The M41S family of mesoporous silicate molecular sieves, developed in 1992, has opened up new possibilities in the fields of catalysis, sensors, and adsorbents (*20*). These materials are synthesized with a self-assembled molecular array of surfactant molecules as a structure-directing template, which results in very sharp and ordered pore distributions of inorganic materials as well as a high surface area and pore volume. These materials can be classified by pore structures as follows: MCM-41(two-dimensional hexagonal mesopore structure), MCM-48 (three-dimensional cubic mesopore structure), and MCM-50 (lamellar mesopore structure). The newly developed mesoporous silica molecular sieve SBA-15 was successfully synthesized using amphiphilic triblock copolymers as a structure-directing template agent under hydrothermal conditions. It has uniform twodimensional hexagonal (space group *p6mm*) mesopore channels that can be tailored by changing synthesis conditions (*21*). Compared with the M41S types, the mesoporous silica SBA-15 molecular sieve has a higher hydrothermal stability and larger pore sizes (about 50-100Å) without pore expanding chemicals; therefore, it can likely incorporate a large portion of the metal precursor without blocking effects (*21*). In addition, water or ethanol extraction can be applied to recover the pore-forming template for reuse in SBA-15 synthesis due to the weak interaction between twodimensional hexagonal silica and triblock copolymer mesophases (*22*). SBA-15 has a surface area of 600-1000m_2/g and a pore volume of 0.6-1.3 cm_3/g which provide highly active sites for applications to adsorption, catalysis, or sensors (*23*). Through several incorporation techniques, the organic or inorganic materials can be functionalized onto the monolayer of highly ordered nano-structured materials. Figure 1 shows the schematic of the proposed structure of the aluminum impregnated SBA-15. Due to their advanced characteristics, the incorporation of functioning materials for mesoporous materials have so far been spotlighted in terms of synthesis, mechanism, and application (*22, 24-26*).

In this study, the relationship between the type of surface complexation and the rate of adsorption was investigated

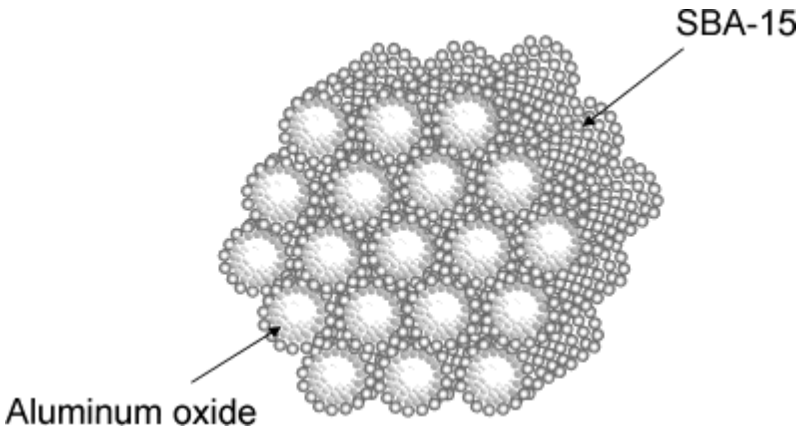

FIGURE 1. Schematic of the proposed structure of the aluminum impregnated SBA-15.

with surface complexation modeling using the constant capacitance model (CCM) for aluminum-impregnated SBA-15 and activated alumina. Because of the unavailability of the extended X-ray absorption fine structure (EXAFS) spectroscopy that can be directly used for experimental investigation of the surface complex structures (*27*), the identity of the complex was ascertained by modeling of the arsenate adsorption edges. In our surface complexation modeling, the oxidation states of metal in the media were modeled with two different site species [monodentate (SOH) and bidentate ($X(OH)_2$)], since our previous results of X-ray photoelectron spectroscopy (XPS) study showed that the oxidation phase of aluminum impregnated SBA-15 was assigned to Al-O which is a lower oxidation state than that of activated alumina (Al_2O_3) (*28*).

The objectives of this study were as follows: (1) to produce adsorbents by synthesizing highly ordered mesoporous silica SBA-15 and incorporating metal oxides onto the SBA-15 surface by use of an incipient-wetness impregnation technique; (2) to evaluate the adsorption of arsenate species onto metal oxide incorporated mesoporous silica; and (3) to investigate the arsenate adsorption behavior of new adsorbents employing the one- and two-site models in surface complexation modeling using CCM.

Methodology

Synthesis of Metal Oxide Impregnated SBA-15. SBA-15 was synthesized using a triblock copolymer (Pluronic P123,EO_{20}-$PO_{70}EO_{20}$, Aldrich) as a structure-directing reagent and tetraethyl orthosilicate (Aldrich) as a silica precursor. Four

grams of the triblock copolymer was dissolved in 60 mL of deionized water for 30 min, and a 2 M hydrochloric acid solution was added. The mixed solution was stirred for 30 min. Tetraethyl orthosilicate (TEOS) was then added to the mixture, and the mixture was heated at 35 °C for 20 h. The mixture was transferred into a Teflon bottle and heated at 80 °C for 24 h without stirring. The solid product was then filtered from the mixture with a 0.45-ím filter and dried at room temperature under vacuum before calcination. The mole fraction of each component for as-synthesized SBA-15 was 1 mol TEOS:5.854 mol HCl:162.681 mol H_2O:0.0168 mol triblock copolymer. Calcination was performed in an oven at 550 °C for 6 h in air to remove the triblock copolymer organic component. The calcined SBA-15 was preserved at room temperature under vacuum. $Al(NO_3)_3â9H_2O$, $Fe(NO_3)_3â9H_2O$, and $Zn(NO_3)_2â6H_2O$ were selected as aluminum, iron, and zinc precursors, respectively, to incorporate metals into SBA-15 through use of an incipient wetness impregnation technique. Each metal precursor was dissolved in the deionized water at given concentrations. The 10% of aluminum impregnated SBA-15 (weight of aluminum/weight of SBA-15) was designated as Al_{10}SBA-15. The mixture was dried in a hood at room temperature for 1 day. All solids were then calcined in an oven programmed to increase the temperature from room temperature to 400 °C at a rate of 0.5 °C per minute, and then hold the temperature for 4 h.. After calcination, the solids were kept inside a vacuum chamber. After synthesizing the media, the conductivity tests were performed to confirm the complete oxidation of the aluminum precursor. Each 0.02 g of media was stirred with 5 mL of deionized water for 10 min and filtered out with a 0.45-ím filter. The conductivity of the filtrate was analyzed with a conductance meter (YSI model 32). The conductivities were below 10 íS/cm, which is the same as that of deionized water, indicating no leaching of aluminum ions.

Characterization of Media. X-ray diffraction (XRD) patterns were obtained using a Stoe High-Resolution X-ray Diffractometer (Microphotonics, Allentown, PA) equipped with CuKR radiation (40 kV, 25 mA) with a 0.05° step size and 5 s step time over the range $0.8° < 2õ < 6.0°$. N_2 gas adsorption *isotherms* were performed at 77Kusing a Micromeritics ASAP 2000 analyzer (Norcross, GA). Media were dehydrated at 250 °Cfor 1 day before performing *isotherm* tests.TheBETspecific surface area was calculated using the linear portion of the

BET equation. The pore size distributions of media were obtained using Barrett, Joyner, and Halenda (BJH) analysis (*29*) of the desorption branch of the hysteresis loop of the nitrogen adsorption *isotherm*. The pore diameter (D_{BJH}), mesopore surface area (A_{BJH}), and volume (V_{BJH}) were calculated from the pore size distribution curve. The pore diameter (D_{BJH}) was calculated using the following equation:

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Arsenate Adsorption *Isotherm* Tests. Sodium arsenate ($Na_2HAsO_4â7H_2O$, Sigma) was used as the arsenate source without any modification. A stock solution of arsenate was prepared at a concentration of 133 mmol/L in deionized water prepared with a Photronix reagent grade water system. $NaNO_3$ (0.01 M) solution prepared with deionized water was poured into a polyethylene bottle of a predetermined volume. Then, a small volume of arsenic stock solution was added to achieve the target arsenate concentration and pH was adjusted with a pHautomatic titrator (Model 48pH 1/16 DIN pHcontroller, EXTECH), using small volumes of acid(HNO_3, 0.1 M) and base (NaOH, 0.1 M) solutions. All samples were mixed in a rotary shaker at 250 rpm and 25 (0.5 °C. After 8 h of shaking, the pH of the samples was readjusted with the automaticpHtitrator. All samples were then shaken again in the rotary shaker until equilibrium was reached. After 24 h of shaking, 5 mL was withdrawn and filtered with a 0.45-*í*m Uniflo filter unit. All data of the arsenic adsorption *isotherm* were fitted with *Freundlich* and *Langmuir isotherm* models. The *Langmuir isotherm* is expressed as follows.

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where Q_{max} (mmol/g) is the maximum adsorption capacity corresponding to complete monolayer coverage, C_{eq} (mmol/L) is the equilibrium solute concentration, and *b* is the equilibrium constant related to the energy of sorption (L/mmol).

The *Freundlich isotherm* model was also tested to describe the adsorption data. It assumes that different sites are involved with several adsorption energies (*30*).The*Freundlich isotherm* is expressed as follows: